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LOW WATTAGE HYDROGEN-AIR FUEL CELLS

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13. ABSTRACT

Low Wattage fuel cells based on the matrix type phosphoric acid cell are discussed.
Nominal ratings of 5-watts or less are considered. Bottled hydrogen or metal hyydrides are used as fuel.
Two approaches are taken. One relying on a conventional bipolar cell design with water removal by the air stream.
In an alternate approach, metal hydrides are integrated with the fuel cell into a device resembling a primary battery. Hydrogen is generated by reaction of the hydride fuel with the fuel cell product water.
Power sources based on the phosphoric acid cell exhibit favorable life characteristics and power densities comparable to or exceeding low rate primary batteries.

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SUMMARY

Contract DAAK02-72-C-0474 was concerned with the development
of low wattage fuel cells based on the phosphoric acid matrix
cell type. Bottled hydrogen or metal hydrides are considered
as fuel sources.

Hydrogen-Air Cell

A self-contained hydrogen-air system nominally rated at 5 Watts
was fabricated and evaluated under the program. A conventional
bipolar cell design with water removal by the cathodic air stream
is relied upon. For start-up and temperature maintenance an
electric heater attached to the cell stack and operated by the
fuel cell output is utilized.

The system is suitable for long life emissions and is operable
over a range of ambient temperatures. With bottled hydrogen,
power densities comparable to low rate primary batteries, for
example the zinc-air depolarized cell, are attainable. Cost per
KWH, however, is considerably lower.

Hydride Cell

Metal hydrides are a unique high energy density fuel for low
wattage fuel cell devices. Clean hydrogen is readily formed by
reaction with water or water vapor. When the hydride is integrated
with the fuel cell the product water itself can be utilized for
hydrogen generation. The latter approach was taken under this
contract. The fuel is integrated with the phosphoric acid fuel
cell into a configuration largely resembling a primary battery.
Operating characteristics and current limiting factors were
examined.

Product water is utilized for hydrogen generation and diffusion
is relied upon for reactant transport.

Very high energy densities are attainable with hydride cells at
room temperatures and low discharge rates. Current densities
and capacity are limited by water transport through the electrolyte
matrix and the hydride bed.

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1.0 INTRODUCTION

Contract DAAK02-72-C-0474 is concerned with the use of the phosphoric acid matrix cell in low wattage devices. Energy levels ranging from fractions of a watt to tens of watts are primarily considered. Fuel cells offer an advantage in this power range based on energy density, cost per KWH or storage characteristics etc. A drawback is their comparative complexity. As a result they lack the operating and handling simplicity of batteries.

The phosphoric acid cell is of promise in this respect. The simplicity of its mass and energy balance minimizes the number of auxilliary components. The cell type has been developed in recent years to considerable degree of perfection and large power plants have been fabricated (1). The phosphoric acid cell is a hydrogen consuming cell and its applicability hinges on a suitable hydrogen source. We have considered in this program bottled hydrogen as a means of fuel storage. This mode of storage appears practical for some applications particularly in view of new developments which may improve the storage density significantly (2). A second source of hydrogen considered - its applicability is likely to be much broader than that of bottled hydrogen - are metal hydrides. These materials deliver large volumes of hydrogen by reaction with water or water vapor and can be handled with comparative ease and safety. Pertinent data for several hydrides are listed in Table 1. The amount of hydrogen derived from a given weight and volume is several times that of bottled hydrogen.

Metal hydrides are a convenient source of gaseous hydrogen. Hydrogen is readily formed for instance by reaction with water in a Kipp Generator. The hydride can also be integrated however with the fuel cell into a configuration largely resembling a primary battery (3). In this case, the product water of the fuel cell is used for hydrogen generation. This type of Integral Hydride cell operates at ambient temperature and relies on reactant transport by diffusion.

TABLE 1 - PROPERTIES OF METAL HYDRIDES

		g/l H_2	Ampere Hrs/g	Watt Hrs/g*	g/cm^3 Density	Available Size
Lithiumhydride	LiH	0.355	6.74	5.39	0.78	Crystalline Powder
Calciumhydride	CaH_2	0.039	2.55	2.04	1.90	Powder, Lumps
Lithiumaluminum-hydride	$LiAlH_4$	0.423	5.65	4.52	0.917	Powder, Pellets
Lithiumborohydride	$LiBH_4$	0.243	9.83	7.86	0.66	Hygroscopic Powder
Sodiumhydride	NaH	1.071	2.23	1.73	1.36	Oil, Suspension
Potassiumboro-hydride	KBH_4	0.602	3.97	3.13	-	-
Hydrogen **	H_2	-	0.208	0.166	-	-

*Based on 0.8V H_2-O_2

** 1A Cylinder,2200 PSI

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2.0   PHOSPHORIC ACID MATRIX TYPE FUEL CELL

Cell components used in this program have been developed largely under previous contracts (4). Component description and relevant performance data are given below.

2.1   ELECTRODE AND MATRIX

Electrodes are based on Teflon impregnated VDL(*) carbon paper activated on one surface with platinum catalyst. Electrodes are combined with a microporous matrix material impregnated with phosphoric acid to a cell. The matrix consists of stabilized Teflon gel with a pore volume of 55-60%. The thickness of the matrix is 0.55 mm and that of the electrodes, 0.3 mm. The matrix "as prepared" is impregnated with 95-100% phosphoric acid. The acid concentration during operation is dependent on conditions and cannot be defined with certainty. A range of 75-98% is probable under the conditions used in this program.

2.2   CELL RESISTANCE

Resistance data for the matrix-electrode laminate covering temperatures from 0-250°F are given in FIG. 1. Measurements were made on test cells with 56 cm^2 area using a Keithley Milliohmmeter Model 502. The test fixture has been described previously (5). Resistance data are given for cell units "as prepared" and after equilibration over calcium hydride. The values include a fixed resistance component of 0.11 Ω cm^2 consisting of contact resistance and resistance of the electrode structure. Cell resistance is strongly temperature dependent and increases sharply at about room temperature. This coincides with the solidification of the electrolyte. Conduction, nevertheless, is sufficient to sustain practical current densities even at temperatures well below freezing.

2.3   SINGLE CELL PERFORMANCE

Performance data for cell components discussed under 2.1 are available primarily for temperatures of 250°F or above (4). This range is preferred in larger power plants because of heat and water removal requirements. Polarization data covering the wider temperature range which is of interest under this program are given in FIG.2. At low temperatures current densities comparable to low rate primary batteries are sustainable. Single cell degradation data for temperatures below 250°F appear in Table 3. Performance stability is excellent in the temperature range of interest for low wattage hydrogen-air cells. The test fixture referred to previously (5) was used in the life evaluation of single cells.

CELL RESISTANCE AS FUNCTION
OF TEMPERATURE

CELL AREA $56\,cm^2$
MATRIX $0.55\,mm$
$\triangle$ AS PREPARED
$\circ$ EQUILIBRATED OVER CaH_2

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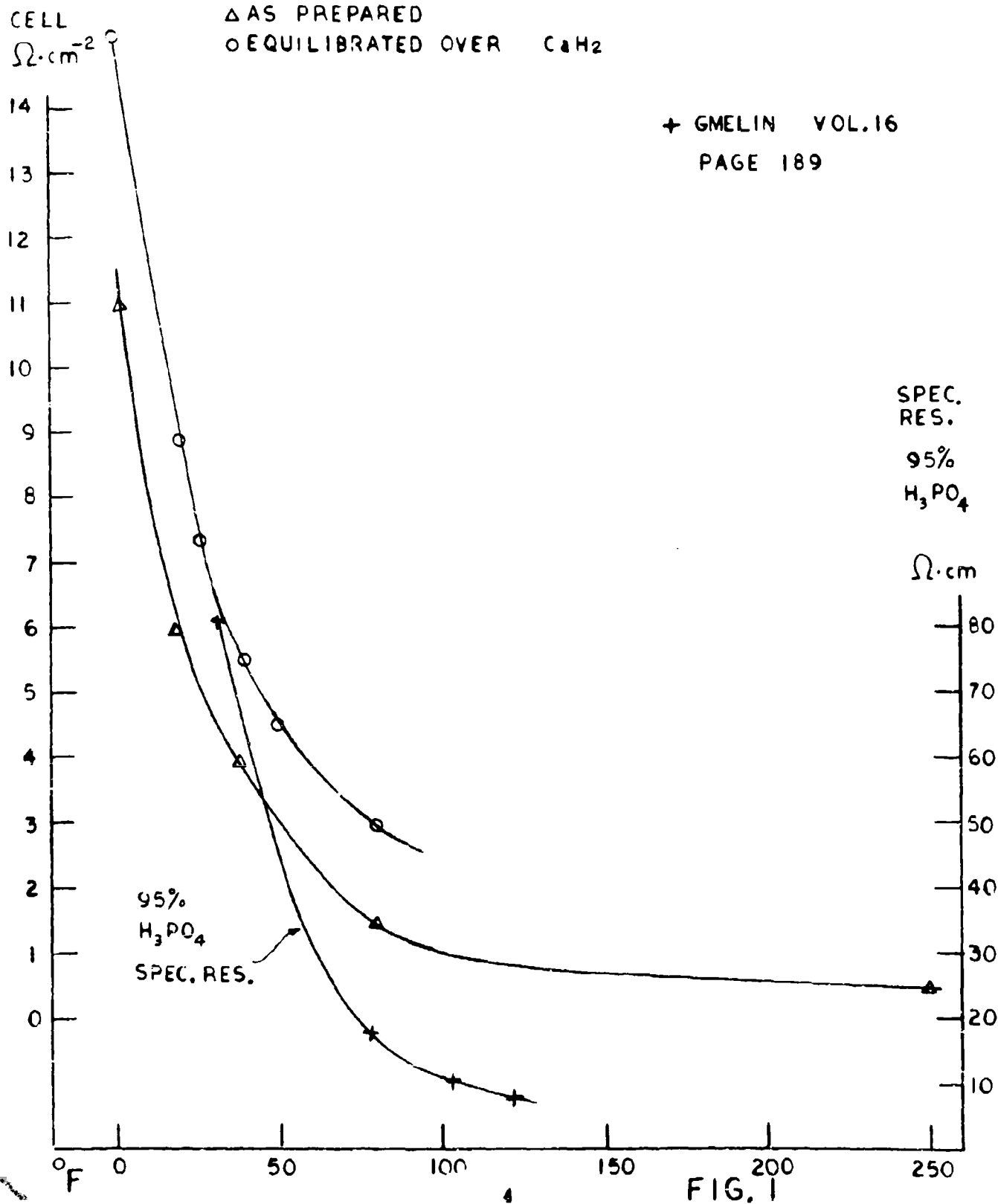
FIG. 1
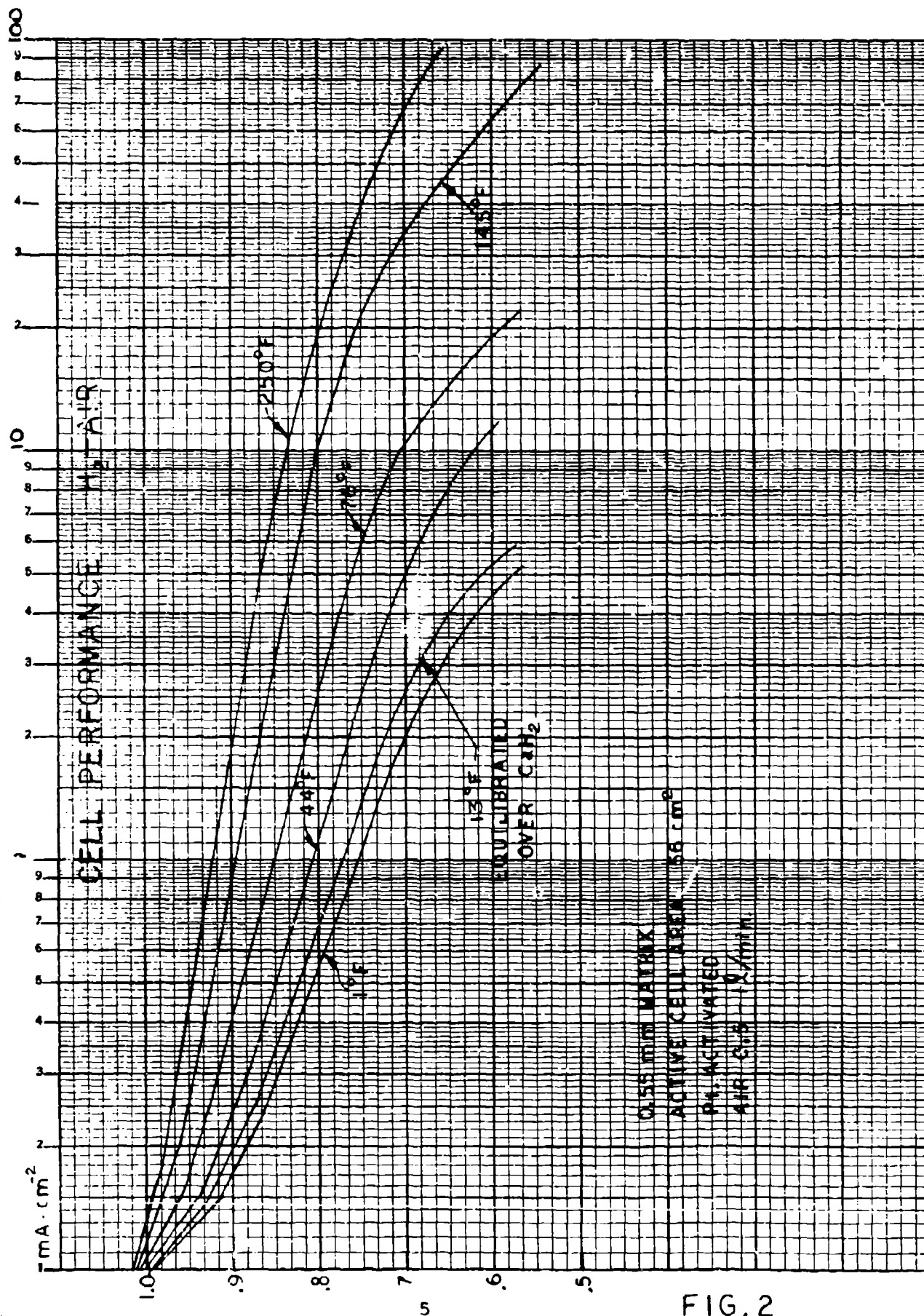
FIG. 2

TABLE 3   LIFE DATA FOR HYDROGEN-AIR CELLS AT
              TEMPERATURES BELOW 250°F

Active Cell Area   :   56 cm^2
Cell Current   :   5A
Air Flow   :   0.8 l/min.

Hours	°F	mV	R Ω
0	196	615	0.0175
48	200	618	
173	203	620	
298	200	617	
516	205	628	0.0160
713	200	618	
910	207	632	
1248	207	631	0.0135
16	160	561	0.0185
217	160	560	
490	161	562	0.0173
780	160	558	
1208	163	559	0.0179

3.0   LOW WATTAGE HYDROGEN-AIR CELL WITH CATHODIC WATER REMOVAL

If gaseous hydrogen is to be used as fuel, a conventional hydrogen-air cell design is a logical approach for a low wattage device. The cathodic air stream is relied upon in this case for product water removal. Elevated operating temperatures are required. A device rated at 5 watts was designed, fabricated and evaluated using this approach. Pertinent information is summarized in the Appendix. A bipolar stack construction with external hydrogen and air manifolding was used. Th general implications of cathodic water removal as applied to low wattage devices and supporting test data are discussed below.

3.1   WATER BALANCE IN SMALL STACKS

For balanced operation of the matrix type phosphoric acid cell a concentrated electrolyte is required. Elevated operating temperatures and high air flow rates assure immediate product water removal. These conditions are not as readily maintained in small devices as in larger system since heat losses rather than heat removal are a concern.

Dilution of the electrolyte due to product water retention is a major concern. The void volume available in the electrode or matrix provide little leeway for changes in electrolyte volume. Upon dilution, the electrolyte penetrates the electrode irrevercibly. Loss of electrolyte due to transient water accumulation may render the cells inoperative. Cross leakage develops once the water is removed from the electrolyte remaining in the matrix.

The relationship between acid concentration, temperature and air flow (expressed as multiples of the stoichiometrically required flow) is illustrated in FIG. 3.

The data indicate the need for large air flow rates and temperatures well in excess of 120°F for the maintenance of high acid concentrations.

3.1.1   THERMAL CYCLING TESTS

A study was performed to determine the capacity of various electrode materials including those discussed in Section 2.1 to contain increases in electrolyte volume during prolonged operation at low temperatures. Comparative tests were carried out in single cells as well as small stack assemblies. Open circuit voltages were recorded to indicate the degree of cross leakage. Single cell test data appear in Table 3. The cells were operated first at low temperatures overnight (at 5A 88 mA.cm^{-2}) and air flow rates of 0.8 1/min (8.5 times toichiometric air flow). Subsequently, the temperature was increased gradually and the open circuit voltage recorded.

A significant increase in cross-leakage apparently takes place under the stated conditions. There is no apparant difference between the electrode samples studied in the capability to contain increases in electrolyte volume. A higher air flow rate corresponding to 17 times the stoichiometric flow was used in tests with stack assemblies. Test data are compiled in Table 4. The stack was loaded with a 4Ω resistor and temperature cycled with an external heater between $265^{\circ}F$ and progressively lower operating temperatures. No decay in the open circuit voltage is observed at this increased air flow rate at operating temperatures above $162^{\circ}F$.

3.2 THERMAL BALANCE IN SMALL STACKS

Under most operating conditions, the waste heat generated in a stack of a few watts rating as considered in this program is insufficient for temperature maintenance. Even with compact stack configurations heat losses are high since stacking, sealing and packaging requirements add significantly to overall dimensions.

Further, geometric limitations are imposed by the need for low pressure drop and adequate reactant distribution.

An auxilliary heat source is required for temperature maintenance. Catalytic heaters in which part of the fuel is burnt or electric heaters operated from the fuel cell are possible approaches.

An electric heater was used in this program because of the ease and precision of temperature control.

TABLE 3   OPEN CIRCUIT VOLTAGES AFTER LOW TEMPERATURE OPERATION

Active Area   :   56 cm^2 Test Fixture see Ref. 5
H$_2$ Flow as required
Air Flow 0.8 l/min^{-1} Relative Humidity estimated
                                      at less than 60%.

Standard	°F	139	185	204	227	238	
Cell mV	O.C.V.	1007	961	947	878	868	(1)
Metallized	°F	154	176	202	–	234	
Teflon							(2)
Electrodes	O.C.V. mV	1010	995	905	–	865	
Standard	°F	157	207	233		237	
Cell with							(3)
increased mV	O.C.V.	1020	999	889		876	
Catalyst							
Loading							

(1)   After 16 hours at 139°F, Current 5A
(2)   After 16 hours at 154°F, Current 5A
(3)   After 16 hours at 157°F, Current 5A

TABLE 4   THERMAL CYCLING TESTS WITH 12-CELL STACK ASSEMBLY

Active Area Per Cell, 25 cm^{-2}
Stack Dimensions
Air Flow Rate 6 l/min.   Hydrogen Pressure Atmospheric

°F	O.C.V.	Remarks
220-240	11.9V	As fabricated
257-265	12.0V	After 8 hours at 184-190°F, 1.68A, 7.13V
237-250	12.0V	After 8 hours at 172-5°F, 1.66A, 7.07V
275-260	12.0V	After 8 hours at 160-163°F, 1.58A, 6.90V

EQUILIBIUM ACID CONCENTRATION AS FUNCTION OF AIR FLOW AND TEMPERATURE

FIG. 3
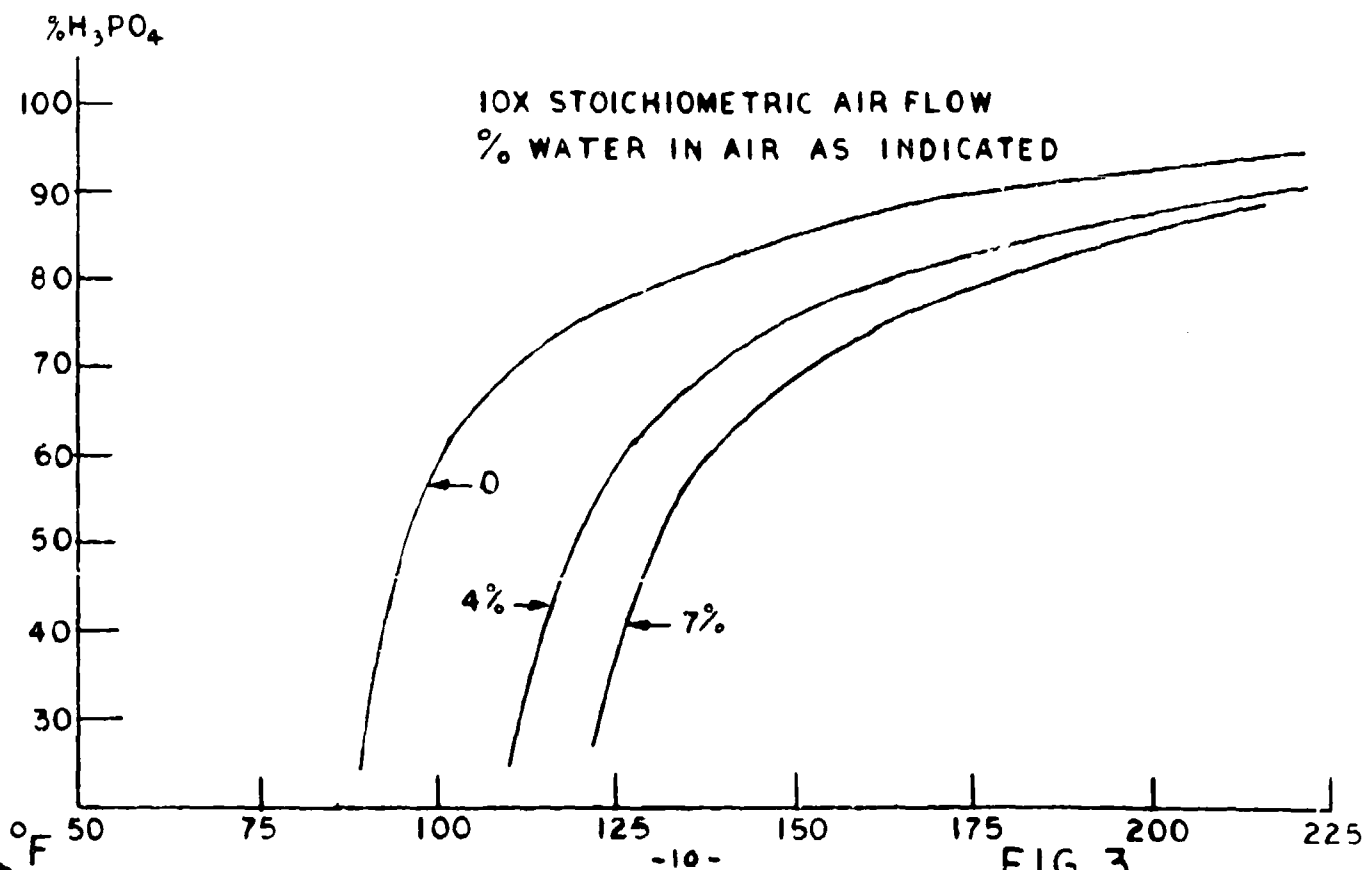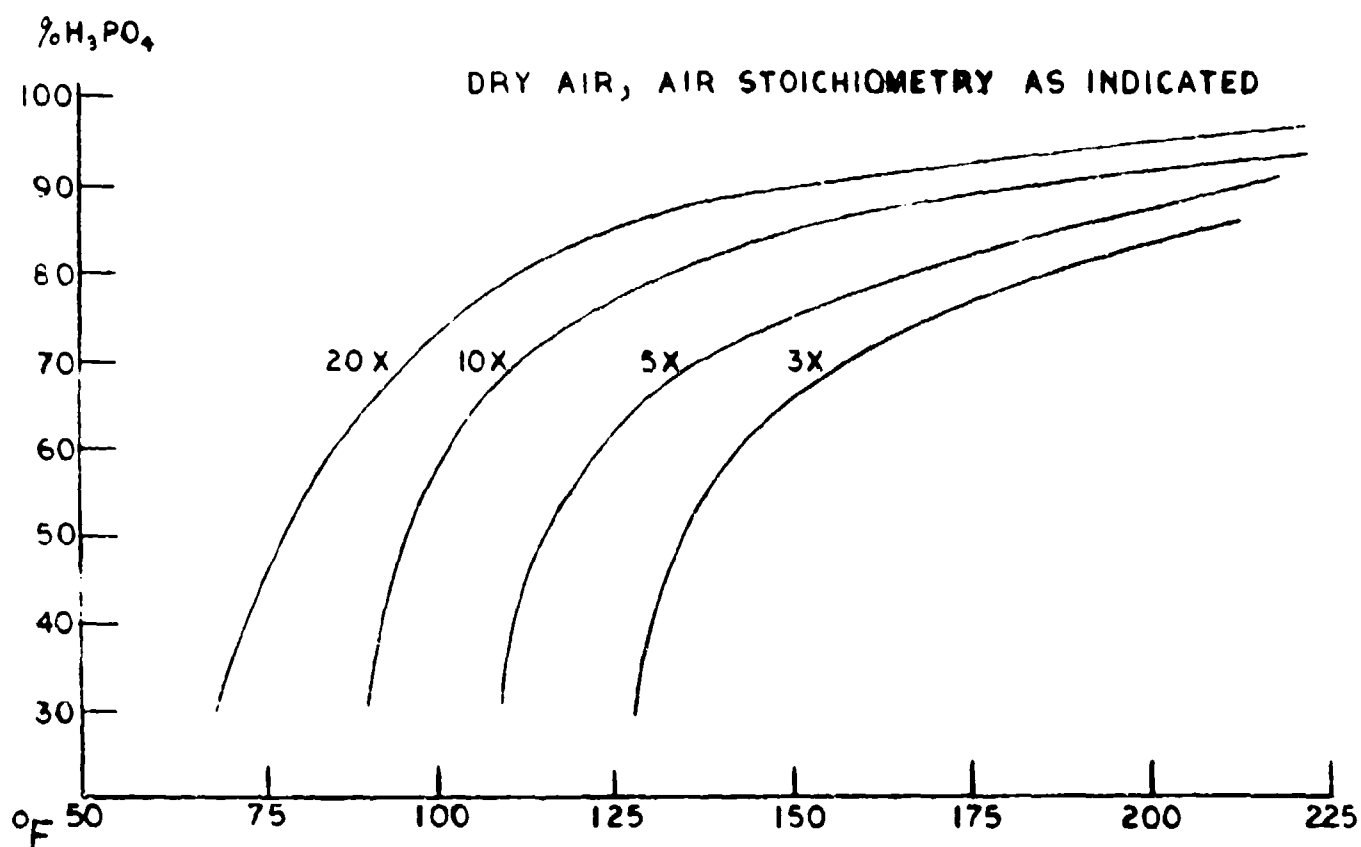
5. CONCLUSIONS

5.1   LOW WATTAGE CELL WITH CATHODIC WATER REMOVAL

The conventional matrix type phosphoric acid fuel cell
with cathodic water removal is suitable for low wattage devices.
An auxilliary heater is needed however for operation since heat
losses exceed the available waste heat under most modes of
operation. An electrical heater attached to the cell stack and
operated by a thermistor controlled circuit was suitable for
temperature maintenance.

Start-Up: Start-up of a low wattage system is possible
by "bootstrapping" with the electrical heater, provided the stack
is at or above room temperature. At low ambient tempertures
water retention can lead to permanent damage of the cells. Under
these conditions power should be provided for start-up from an
external source.

Operating Temperature: A minimum operating temperature of
$150^{\circ}F$ and high air flow rates are required to assure product
water removal.

Thermal Efficiency: Thermal efficiency largely depends on
the auxilliary heat requirements for temperature maintenance.
Operation at rated load is desirable to increase the available
waste heat.

5.2   INTEGRAL HYDRIDE CELL

The integration of metal hydrides with the phosphoric acid
cell for the purpose of utilizing the product water for hydrogen
generation is an intriguing concept. Hydride cells are comparable
to primary batteries in operational simplicity but exhibit signi-
ficantly higher energy densities. The following conclusions can
be drawn from investigations performed.

Current Efficiency and Energy Density: Single cell
discharge experiments with CaH_2 and $LiAlH_4$ at room temperature
indicate current efficiencies of 78.7 to 88.6%. Based on these
data energy densities in excess of 1 WHr/g are attainable in
practical cells. The efficiency loss is attributed primarily to
leakage and incomplete fuel conversion. Cross-leakage of
reactants through the matrix appears comparatively small but may
be a significant factor at low discharge rates.

Material Balance: The relative amount of hydrogen generated
in the reaction of product water with the metal hydride is the
main consideration in the material balance. With calcium hydride,
the product water from the fuel cell is insufficient to replenish
the hydrogen consumed. Experiments discussed in Section 4.3

indicate a deficiency of 4-6%. Make up water or hydrogen are required with this fuel to sustain cell operation. A possible source of make up water is the moisture in the air.

With $LiAlH_4$ an excess of hydrogen is available(at least at room temperature) if all product water is reacted with the fuel. The material balance is maintained in this case by the venting of hydrogen from the fuel compartment or the dissipitation of water through the cathode into the air stream.

Current Limiting Factors: The current density in a hydride cell is predominately determined by the rate of water diffusion from the cathode to the hydride fuel. Initially, water transport through the electrolyte matrix is current limiting. As more of the fuel is consumed however, and the length of the diffusion path increased, water transport through the converted fuel becomes current limiting. Hydrogen generation experiments with CaH_2 and to a lesser extent with $LiAlH_4$ indicate an inverse proportionality between the rate of hydrogen generation and the total volume of hydrogen generated. The data indicate that current densities in excess of 1 mA/cm^2 should be sustainable for more than a year at room temperature.

Water transport through the matrix is not proportional to the partial pressure of water nor the thickness of the matrix. A diffusion barrier appears to develop at the interface between the matrix and the hydride bed because of water depletion.

Low Temperature: Experimental data currently available are insufficient to assess the temperature limits for the operation of hydride cell. Current-potential measurements with hydrogen indicate that operation of the phosphoric acid cell itself is feasible at temperatures well below freezing. More information is required however on the rate of hydrogen generation from hydride beds at low temperatures as well as the magnitude of reactant loss due to cross-leakage.

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4.0   LOW WATTAGE CELL WITH INTEGRAL HYDRIDE FUEL

Metal hydrides as indicated before can be readily converted into hydrogen gas by reaction with water, for instance, in a Kipp Generator. The use of these compounds, however, is not necessarily limited to this approach.

Hydrides can also be integrated with the fuel cell into a configuration in which product water from the cell is utilized for hydrogen generation. The hydride in this case is not only a source of fuel but also serves to maintain the water balance since the product water is consumed. This novel concept is exceedingly attractive(3). The Integral Hydride cell is simple in its operation and power densities compare favorable to primary batteries at medium to low discharge rates. No bulk liquids are required since the electrolyte is well contained in the matrix. Reaction products are solid.
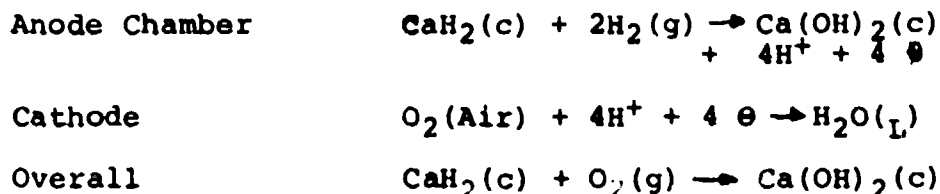
A series of single cell experiments was performed with hydrides to determine the general discharge characteristics. This study was followed by an examination of the current limiting steps and the fabrication of a 0.5 watt device which was delivered to the contractor.

4.1   PRINCIPLE OF INTEGRAL HYDRIDE CELL

The principle of operation of an integral hydride cell is shown in FIG. 4.

The hydride is located in sufficient proximity of the electrodes that diffusion of water vapor can be relied upon for water transport.

The high reactivity of certain hydrides even at low temperatures towards water vapor leads to a water vapor gradient which serves as a driving force. With calcium hydride, a preferred fuel the overall reactions involved are as follows:

Anode Chamber
$$CaH_2(c) + 2H_2(g) \rightarrow Ca(OH)_2(c) + 4H^+ + 4\, \ominus$$

Cathode
$$O_2(Air) + 4H^+ + 4\, \ominus \rightarrow H_2O(_L)$$

Overall
$$CaH_2(c) + O_2(g) \rightarrow Ca(OH)_2(c)$$

The current limiting factor in this cell is primarily the rate of water transport.

4.2   SINGLE CELL DISCHARGE EXPERIMENT

Calcium hydride and lithium aluminum hydride, both very reactive towards water vapor were used as fuels in initial experimentation. Single cell discharge tests performed with these
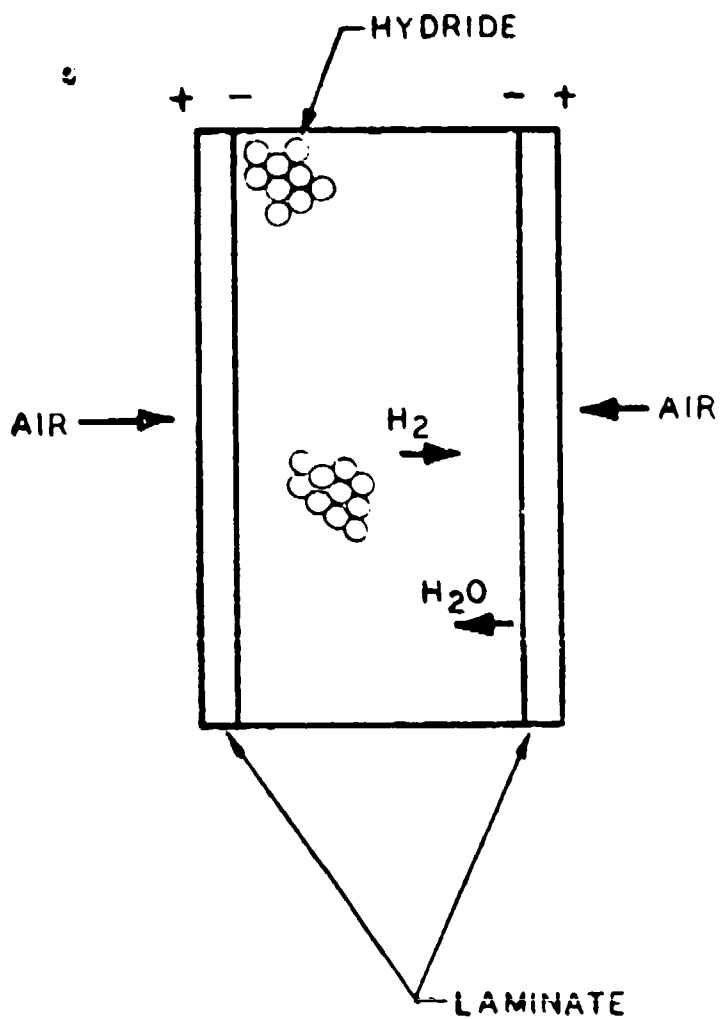
FIG. 4   PRINCIPLES OF OPERATION OF INTEGRAL

HYDRIDE FUEL CELL

fuels served to determine the general discharge characteristics and the current efficiency. Further information was obtained regarding the volume and weight changes of the fuel charge which occur as the hydride is converted to oxides or hydroxides in the course of the disbharge.

Most experimentation was performed in Plexiglass cells with 19.6 cm^2 active cell area. Air was supplied by diffusion. The electrode-matrix laminate was supported by screens reinforced by a 1.25 cm thick layer of Honeycomb support. The hydride was separated from the anode by a sheet of fiberglass paper.

Cells were discharged at a constant voltage of 0.72 volts and the current was continuously recorded. Data are summarized in Table 6. Current densities of about 4 mA cm^{-2} can be sustained with calcium hydride or 7 mA cm^{-2} with lithium-aluminum-hydride. Current efficiency is in excess of 80%.

Hydrides expand considerably upon reaction with water vapor. In the case of calcium hydride the volume increases by 60%. The corresponding increase with Lithium aluminum hydride is about 120%.

4.2.1 WATER REQUIREMENT FOR HYDROGEN GENERATION FROM HYDRIDES

The material balance for the integral hydride cell is discussed in Section 5-2. An important aspect of the overall material balance is the amount of hydrogen generated from each mol of product water. This ratio was determined for a number of hydrides. Samples were placed in a Plexiglass tube, sealed with a thin porous Teflon membrane and exposed to water vapor. The evolving hydrogen was collected in a burrette. The H_2/H_2O ratio was then determined from the weight gain of the hydride sample corrected for the released hydrogen. Respective data are summarized in Table 7.

The metal hydrides tested appear "water deficient", that is more water than that available from the fuel cell is required for sustained operation. An exception is Lithium-aluminum hydride which at room temperature yields more than the stoichiometrically required amount. A slight excess of water is also needed with calcium hydride. The deficiency is in the order of 4-6% of the stoichiometrically required amount and appears largely independent of temperature. Calcium hydroxide is formed exclusively in the reaction of calcium hydride with water vapor. No stable hydrates have been reported for calcium hydroxide (6). The water deficiency with this fuel may result from the adsorption of water vapor on the hydroxide powder (7). The H2/H2O ratio observed with LiH, LiAlH$_4$ (at low temperatures) and KBH$_4$ may be misleading because of slow reaction steps and further testing is required.

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TABLE 6   DISCHARGE DATA FOR INTEGRAL HYDRIDE CELLS (1)

Fuel***	Fuel Charge(g)	Ahr. Capacity	Ahr. Obtained	Weight gain(g)	Bulk Density of Converted Fuel g/ml	Average Current mA cm^{-2}	Current* Efficiency %
LiAlH$_4$	12.9	68.5	58.5	16	0.29	5.9	85.4
LiAlH$_4$	10	54.8	48.5	13.4	0.29	7.3	88.5
CaH$_2$	10	23.7	18.6	7.5	0.56	3.7	78.7
CaH$_2$**	10	23.7	21	7.3	0.53	4.2	88.6

(1) Discharge at constant voltage of 0.72V, Matrix 0.55 mm thick.
    Temperature: 70-80°F
    Cell Area : 19.6 cm^2

*Based on 93% purity for CaH$_2$ and 97.5 purity for LiAlH$_4$

**Matrix 0.25 - 0.30 mm thick.

***LiAlH$_4$ Foote Minerals, crushed pellets -4 mesh, bulk density 0.48 g/ml
   CaH$_2$ Foote Minerals, -4 mesh, bulk density 0.85 g/ml.

TABLE 7   **HYDROGEN GENERATION FROM METAL HYDRIDES WITH WATER VAPOR**

	Sample Size(g)	Weight gain(g)	H₂ Evolved (l) 25°C	H₂O Torr	Temp. °C	H₂/H₂O	Remarks
CaH₂	12.3	2.52	3.34	1.63	-12	0.947	-4 Mesh, Foote Mineral
CaH₂	4.7	2.55		1.36	-14	0.938	-4 Mesh, Foote Mineral
CaH₂	9.4	2.83	3.97	23.7	+25	0.957	-4 Mesh, Foote Mineral
LiAlH₄	6.6	3.11	3.91	2.76	-6	0.895	-4 Mesh, Crushed Pellets, Foote Mineral
LiAlH₄	8.6	2.05	3.21	26.7	+27	1.091	-4 Mesh, Crushed Pellets, Foote Mineral
LiAlH₄	7.03	2.86	2.74	2.71	-7	0.699	Ventron, Powder
LiH	10.23	0.778	0.93	26.7	+27	0.85	Ventron, Coarse Crystalline Powder
KBH₄*	14.8	1.74	1.61	30.0	29	0.705	Ventron, Crushed Pellets

*Contains CoCl₂ as decomposition catalyst.

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4.3   WATER DIFFUSION AND HYDROGEN GENERATION EXPERIMENTS

The major current limiting factor in the Integral Hydride cell is the transport of water from the cathode to the hydride fuel.   A series of tests was performed to assess the relative significance of individual components on overall rates of water transfer.

4.3.1 HYDROGEN GENERATION FROM HYDRIDE BEDS

Hydrogen is generated from hydrides by diffusion of water vapor into a packed bed of hydride particles. Obviously, the rate of hydrogen generation diminishes as hydride is converted and the length of the diffusion path increased. Experiments LiH_4 and CaH_2 were performed at 90°F and 76°F.

Tests were carried out in a Plexiglass tube (cross-sectional area 13.6 cm^2) in which the hydride was separated from water or ice by a porous Teflon membrane (0.25 mm,   75% porosity). Hydrogen was collected in a burette. The generation rate measured as a function of time and the cumulative volume of hydrogen generated per unit area.

A sharp interface between reacted and unreacted hydride develops with calcium hydride. A broader Zone of about 5 cm width develops with Lithium-aluminum-hydride. It is comprised possibly of partially reacted hydride. Test results are tabulated in Table 8, 9 and discussed in Section 5.2.

4.3.2 WATER DIFFUSION THROUGH THE MATRIX AND CELL LAMINATE

The generation of hydrogen from calcium hydride with water vapor was used as a tool for the determination of water transport rates through the matrix and the electrode-matrix laminate.

Water transport through standard matrix materials was examined at room temperature in the test set up shown in FIG. 5.

Calcium hydride was placed in one side of the matrix separated from the acid impregnated material by a 0.25 mm thick porous Teflon sheet. On the other side of the matrix a constant water vapor pressure was maintained by a large flow of moist air. The rate of hydrogen generation was determined at various levels of humidity with a matrix of 0.25 and 0.55 mm thickness. Identical experiments were performed with matrix-electrode laminates.

Test results are summarized in FIG. 6 and Table 10.

The data indicate that diffusion through the matrix is considerably slower than through the hydride bed. The electrodes

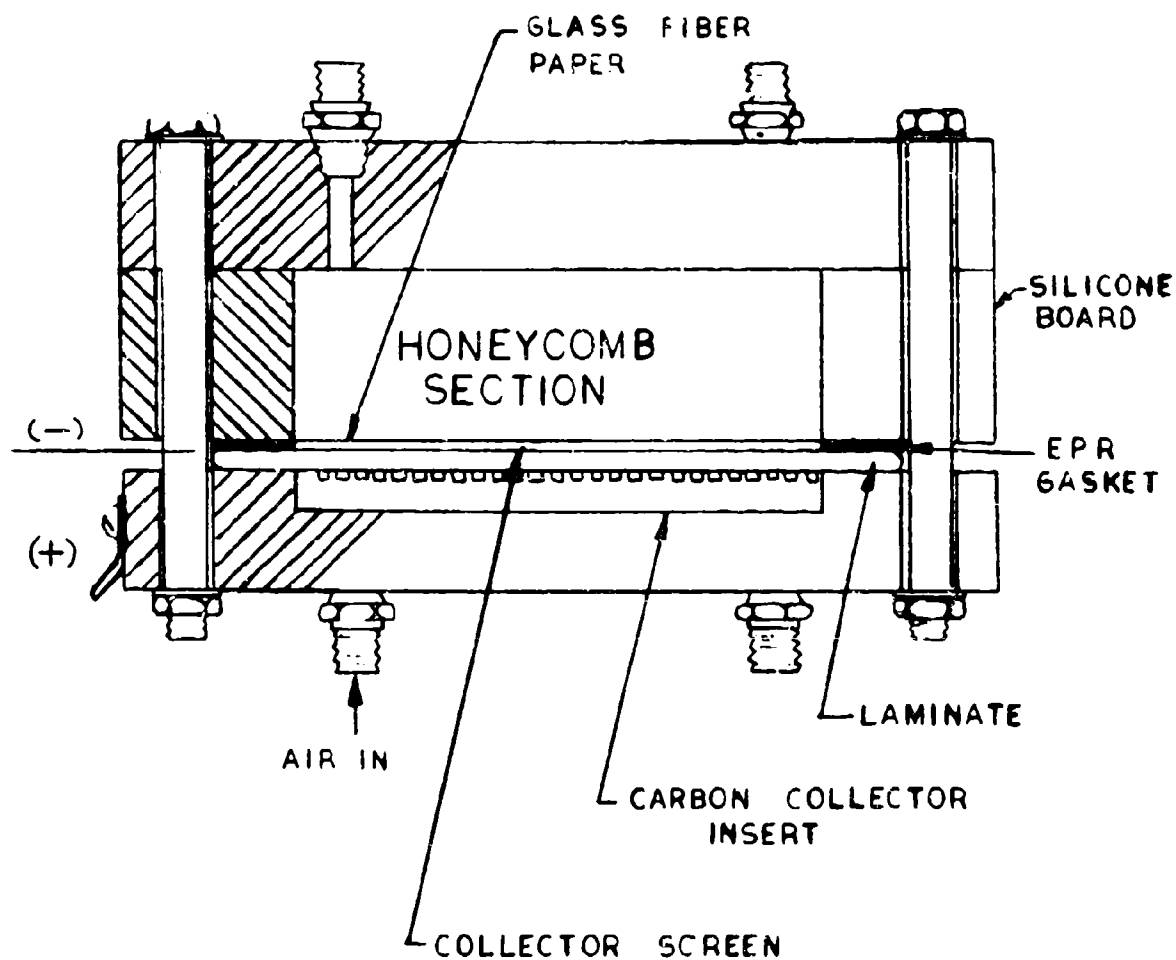# TEST FIXTURE FOR HYDRIDE STUDIES
(ACTUAL SIZE)

FIG. 5

TABLE 13 — HYDROGEN GENERATION WITH CALCIUM HYDRIDE

Calcium Hydride, Foote Minerals, -4 mesh
Cross-Sectional Area of Hydride Bed 19.6 cm^{-2}

$9°F$, P H_2O 0.00226 Atm.

Generation Rate ml.cm^{-2} min.$^{-1}$	0.119	0.048	0.035	0.029	0.024	0.020	0.016	0.013
Total Hydrogen Volume ml cm^{-2}	10.2	127	255	383	510	638	765	893

$76°F$, P H_2O 0.030 atm

Generation Rate ml. cm^{-2} min.$^{-1}$	9.7	4.6	2.9	1.48	0.81	0.56	0.43	0.28	0.15
Total Volume Hydrogen ml. cm^{-2}	-	140	220	350	460	530	630	1000	1610

TABLE 9 — HYDROGEN GENERATION WITH LITHIUM ALUMINUM HYDRIDE

-4 Mesh LiAlH$_4$, Cross-Sectional Area of Hydride Bed 19.6 cm^{-2}

9°F, P H$_2$O 0.00226 Atm.

Generation Rate ml. cm^{-2} min.$^{-1}$	0.187	0.081	0.044	0.029	0.022	0.0178
Total Hydrogen Generated ml.cm^{-2}	10.2	127.5	255	283	510	640

76°F, P H$_2$O 0.030 atm

Generation Rate ml.cm^{-2} min.$^{-1}$	1.2	2.3	2.0	0.95	0.56	0.39	0.28	0.23	0.16	0.135	0.115	0.095
Total Hydrogen Generated ml.cm^{-2}	10	100	200	400	600	800	1000	1200	1600	2000	2400	2800

do not restrict water transport as indicated by the values
obtained for the laminate. Interestingly, the matrix thickness
as well as the partial pressure of water are not directly pro-
portional to the rate of water diffusion. This is taken to
indicate that diffusion through the bulk of the matrix is not
the only and most likely not the major restriction to water
transport. A diffusion barrier appears to develop on the
surface of the matrix facing the hydride bed. This barrier may be
a water depleted acid layer in the matrix which is formed because
of the relatively faster rate of water diffusion in the hydride
bed than in the matrix. Further discussion of these results
is given in Section 5-2.

TABLE 10

<u>WATER DIFFUSION THROUGH H_3PO_4 MATRIX MATERIALS</u>

Cell Area 19.6 or 56 cm^2
Air Flow about 1 ℓ/min.

°F	Rel. Humidity %	P_{H_2O} Torr	ml/min^{-1}cm^{-2} Hydrogen	Equivalent* mA cm^{-2}
Matrix 0.55 ∓ 0.05 mm				
71	100	19.3	0.26	19.2
72	70	14.0	0.24	17.8
71	3?	6.4	0.13	9.6
69	25	4.5	0.11	8.1
Matrix 0.25				
69	100	18	0.36	26.6
70	30	5.6	0.18	13.3
70	20	3.7	0.117	8.6

*1 mA.cm^{-2} equals 7.4 x 10^{-3} ml. min.$^{-1}$cm^{-2}

WATER TRANSPORT THROUGH MATRIX
AND CELL LAMINATE

FIG.6   -24-

LITERATURE REFERENCES

(1)   Open Cycle Fuel Cell Power Plant
        Final Technical Report, Contract No. DAAK02-70-C-0517
        MERDC, Fort Belvoir, Virginia, July 1973

(2)   Privat Communication, Brookhaven National Lab.

(3)   MERDC, Privat Communications

(4)   Phosphoric Acid Fuel Cell Stacks
        MERDC, 1969, Contract No. DAAK02-68-C-0407

(5)   Evaluation of Phosphoric Acid Matrix Fuel Cell,
        Contract No. DAAKO-67-C-0219, MERDC
        Sixth Semi-Annual Report, 1970

(6)   G. F. Huttig, A. Arbes, Z. Anorg. Ch., 191, 1930, 161/70

(7)   V. Rodt Zeitschrift fur Anorganische Chemie 228, 1936,
        175/7

A P P E N D I X

6.0 5-WATT HYDROGEN-AIR CELL

In conformity with the performance objective of contract
DAAK02-72-C-0474 listed in Table A-1 a fully integrated power
source operative on gaseous hydrogen and ambient air was designed,
fabricated and evaluated.

6.1 SYSTEM DESIGN

Pertinent systems design data are summarized in Table A-2.
The major components are a 12-cell stack with electric endplate
heaters, a temperature and voltage control circuit and a blower
assembly.

The systems is housed in a deep drawn aluminum can with
openings for air inlet and air exhaust as well as electrical and
fuel supply connections.

The stack is insulated by 6 mm thick silicon board plates
which also serve as endplates, and hydrogen manifold cover. The
position of the stack in the aluminum housing is secured by
frames.

The blower assembly and electronic board is mounted on the
cover of the housing. The Stack assembly appears in FIG. A-1 and
the total system is shown in FIG. A-2.

Voltage regulation and temperature control circuitry is
shown schematically in FIG. A-3 and an outline drawing of the
entire system appears in FIG. A-4.

6.2 SYSTEMS EVALUATION

Operating characteristics of the hydrogen-air system were
determined over the range of conditions listed below:

Ambient Temperature   : $10^{\circ}F - 132^{\circ}F$

Load   :   0 - 11.3 watts

Hydrogen Pressure   :   Atmospheric to 1 psig

Technical grade hydrogen was used throughout the evaluation. The
air flow controlled by the size of the air inlet and exhaust
opening was set to 4 or 6 l/min. Test data reported below have
not necessarily been obtained from testing of the finalized system
developed under this program.

The information reported nevertheless is considered represen-
tative for this system.

6.2.1 <u>START-UP</u>

The system becomes operative with the admission of hydrogen.
Self-heating commences immediately first by the reaction of
hydrogen with the air present in the fuel cavities (a quick
purge is required to remove the bulk of residual nitrogen) and
then by the heat supplied with the endplate heaters ($8\,\Omega$ each,
connected in parallel) or the waste heat generated by the heater
or any external load current.

The start-up time required to reach 7 volts is shown in
Table A-3 for various operating conditions. Additional data
concerning start-up appear in FIG. A-5 and FIG. A-6.

TABLE A-1   PERFORMANCE OBJECTIVES FOR 5-WATT
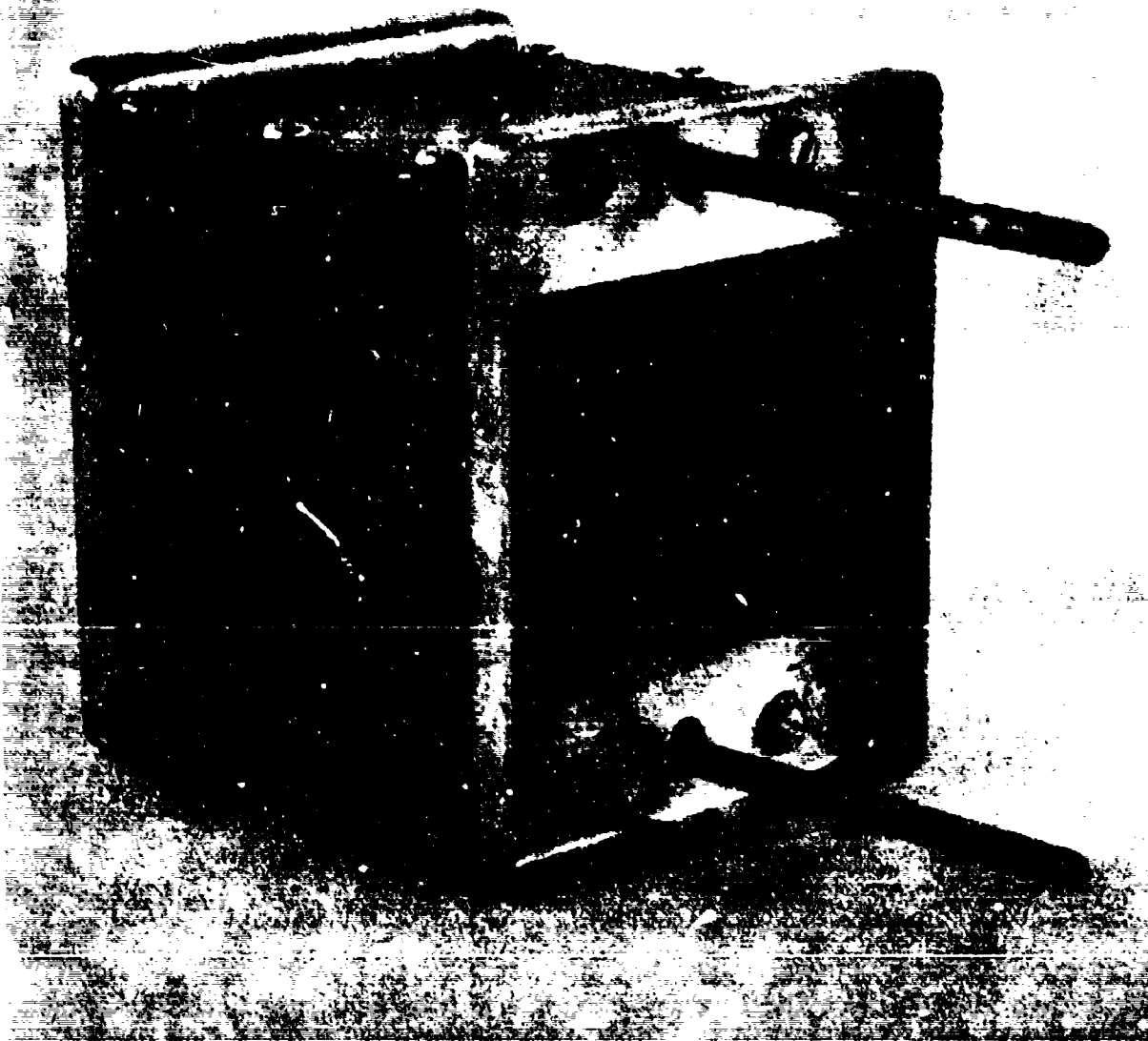   HYDROGEN-AIR CELL

Power Level	5-Watts at 7 volts minimum rated power.
Life	Goal of 9000 hrs.
Operating Temperature	-40°F to 130°F
Fuel	Commercial grade hydrogen, supply pressure 0.5 to 1.5 psig
Operating Environment	Operable burried to 12" deep and above ground to elevations of 8000 ft. in any orientation.
Electrical Response	Output voltage transients not to exceed 30% of steady state voltage upon application or removal of any load up to rated loud.
Size and Weight	Single package with minimum weight and volume.

TABLE A-2   DESIGN SPECIFICATIONS FOR 5-WATT HYDROGEN-AIR CELL

Dimensions, Overall	17 x 8.8 x 10.8 cm
Weight	1.35 kg.
Stack Dimensions	6.9 x 8.8 x 7.8 cm
Number of Cells	12
Active Cell Area	25 cm^2
Stacking Density	2 cells/cm
Air Supply *	Integral blower with constant flow of 6 l/min.
Hydrogen Supply	0.1 - 0.5 psi commercial grade
Hydrogen Bleed Rate	2 ml/min at 0.3 psi
Temperature and Voltage Regulation	See FIG. A-1
Start-Up & Temperature Maintenance	By integral heater, 2 heating pads 8 Ω each.

*Brush Type DC Motor

FIG.A-1   5 WATT HYDROGEN-AIR FUEL CELL STACK
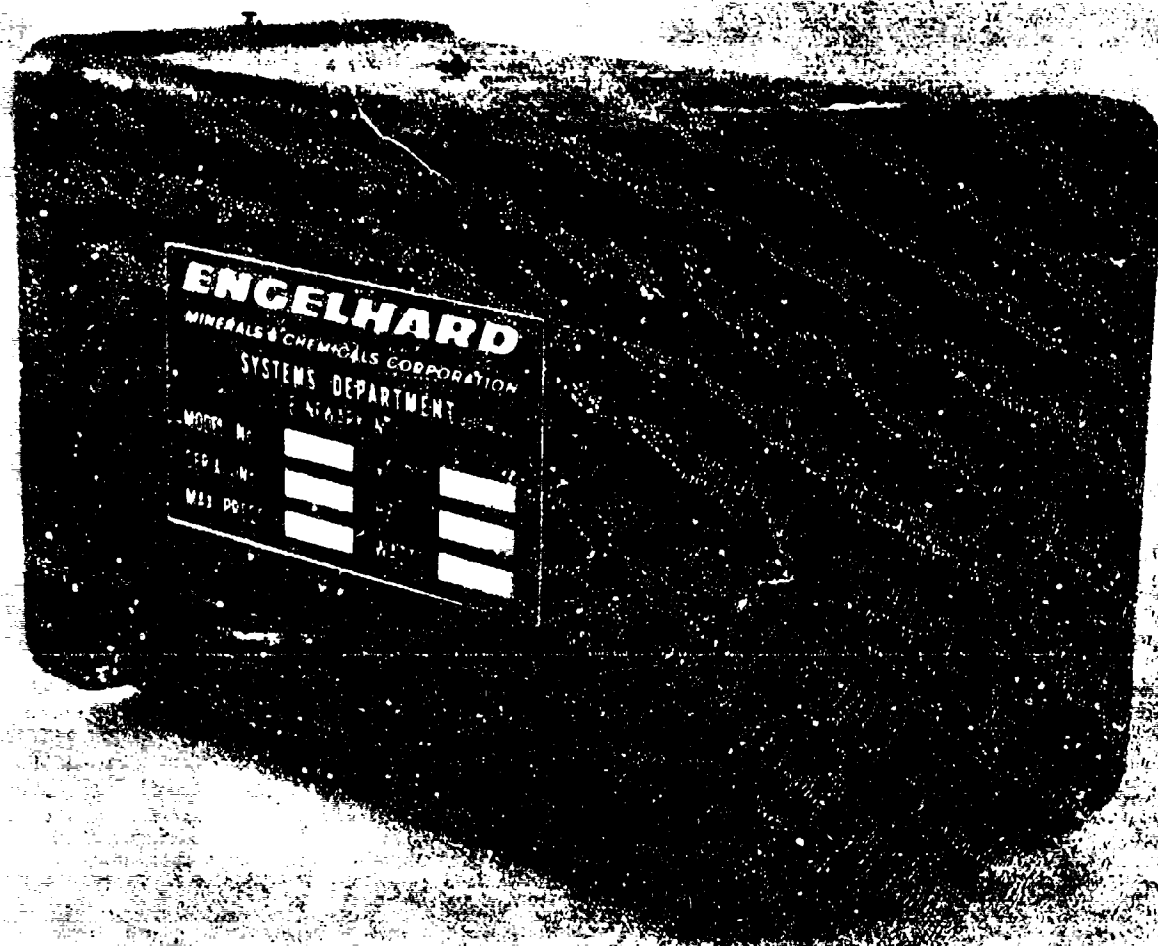
FIG.A 2   5 WATT HYDROGEN -AIR FUEL CELL

TEMPERATURE AND VOLTAGE REGULATION FOR 5 WATT CELL

VOLTAGE REGULATION

TEMPERATURE CONTROL CIRCUIT
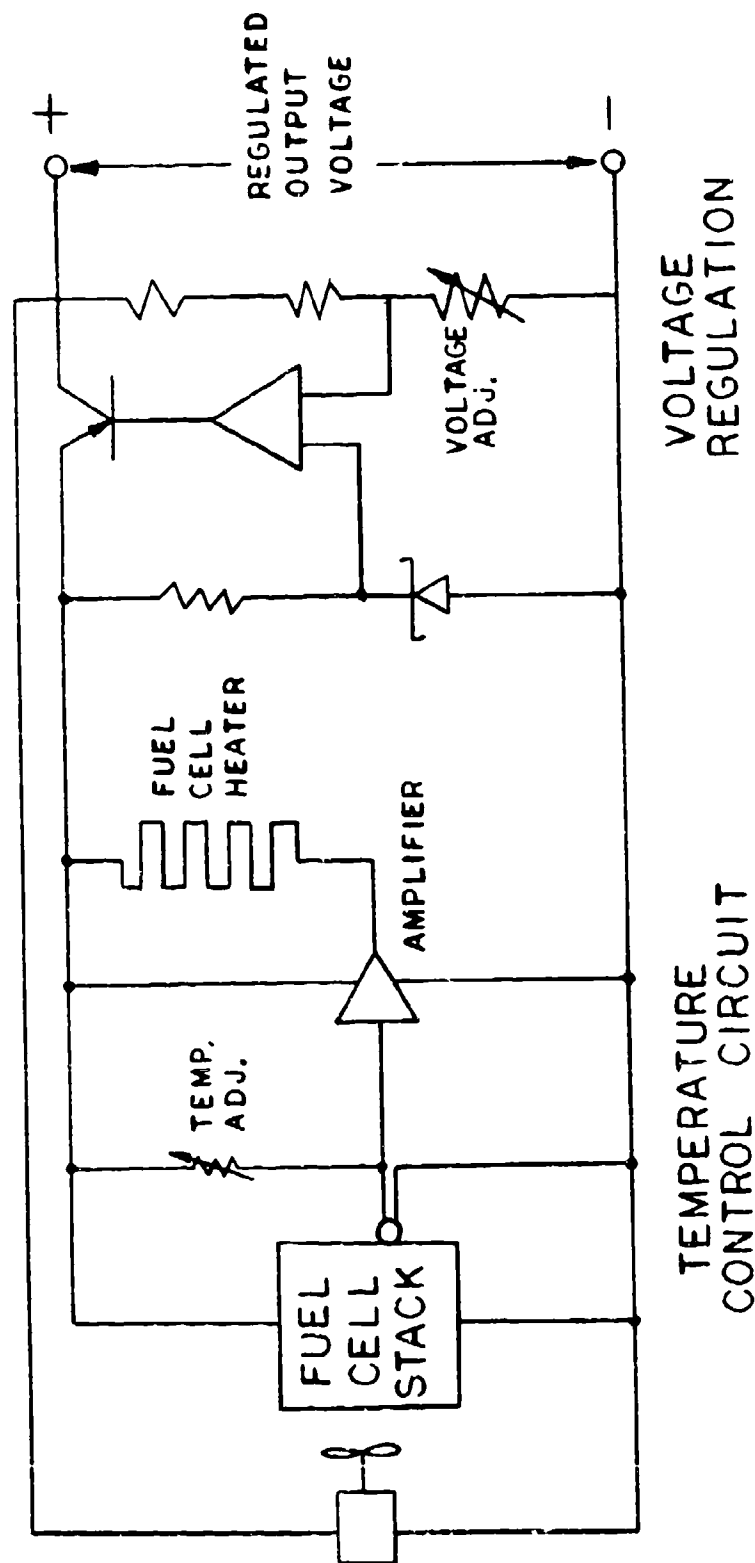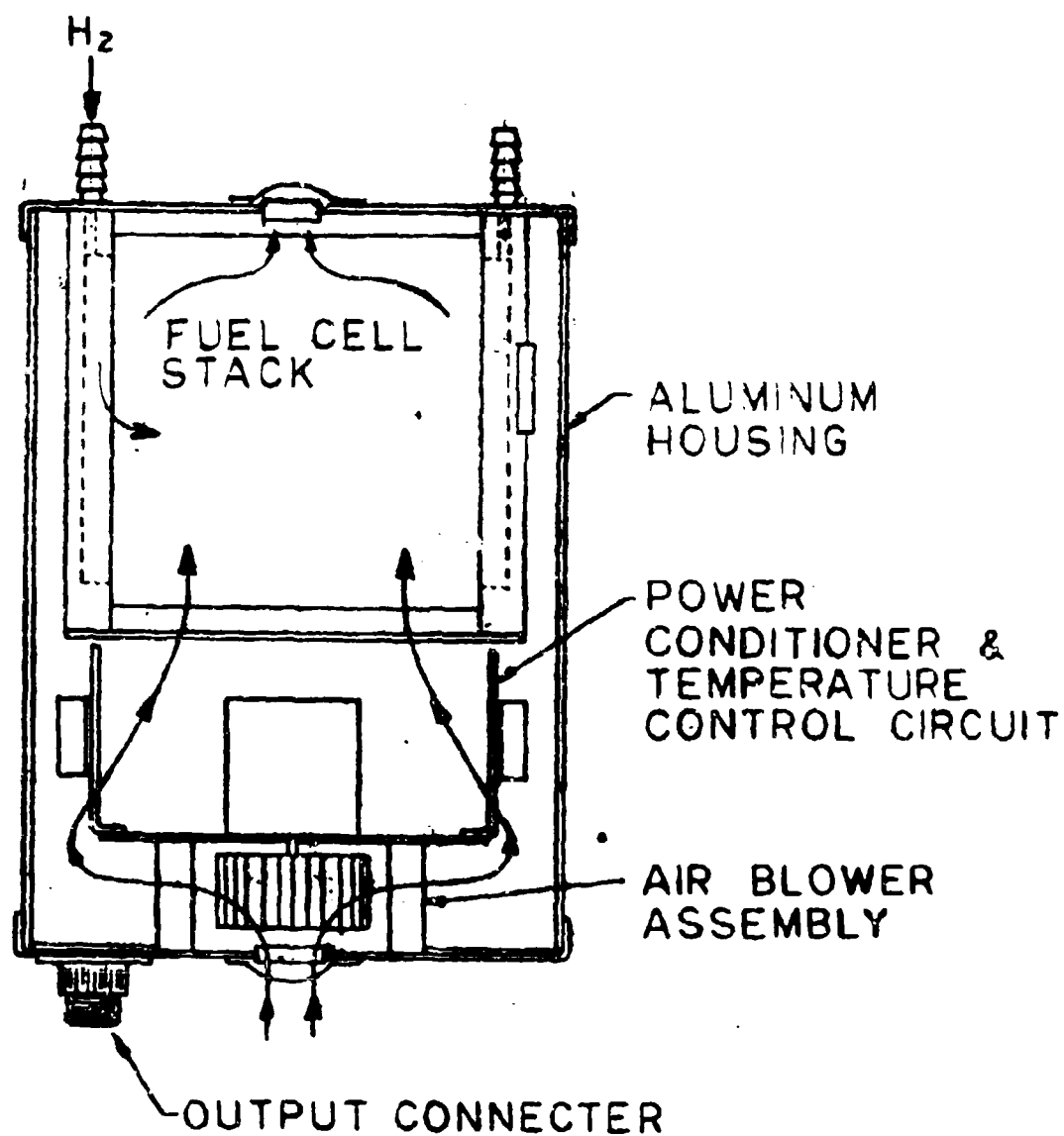
FIG. A-3

FIG. A-4 OUTLINE DRAWING OF 5WATT HYDROGEN -AIR FUEL CELL

TABLE A-3   START-UP TIME FOR HYDROGEN-AIR
                         SYSTEM

Ambient Temperature	Load	Minutes to 7 volts
$10^{O}F \; ^{-0}_{+4}$	10	19
$76^{O}F$	10	4-1/2
$130^{O}F$	10	17 sec.
$76^{O}F$	0	15 sec

COLD START OF
H₂-AIR SYSTEM

CONTROL TEMP. 110°F
LOAD 10 Ω
AMBIENT 10°F

-A 10-

FIG. A-5

COLD START OF H_2—AIR SYSTEM   CONTROL TEMP. 170°F
                                  LOAD   10 Ω
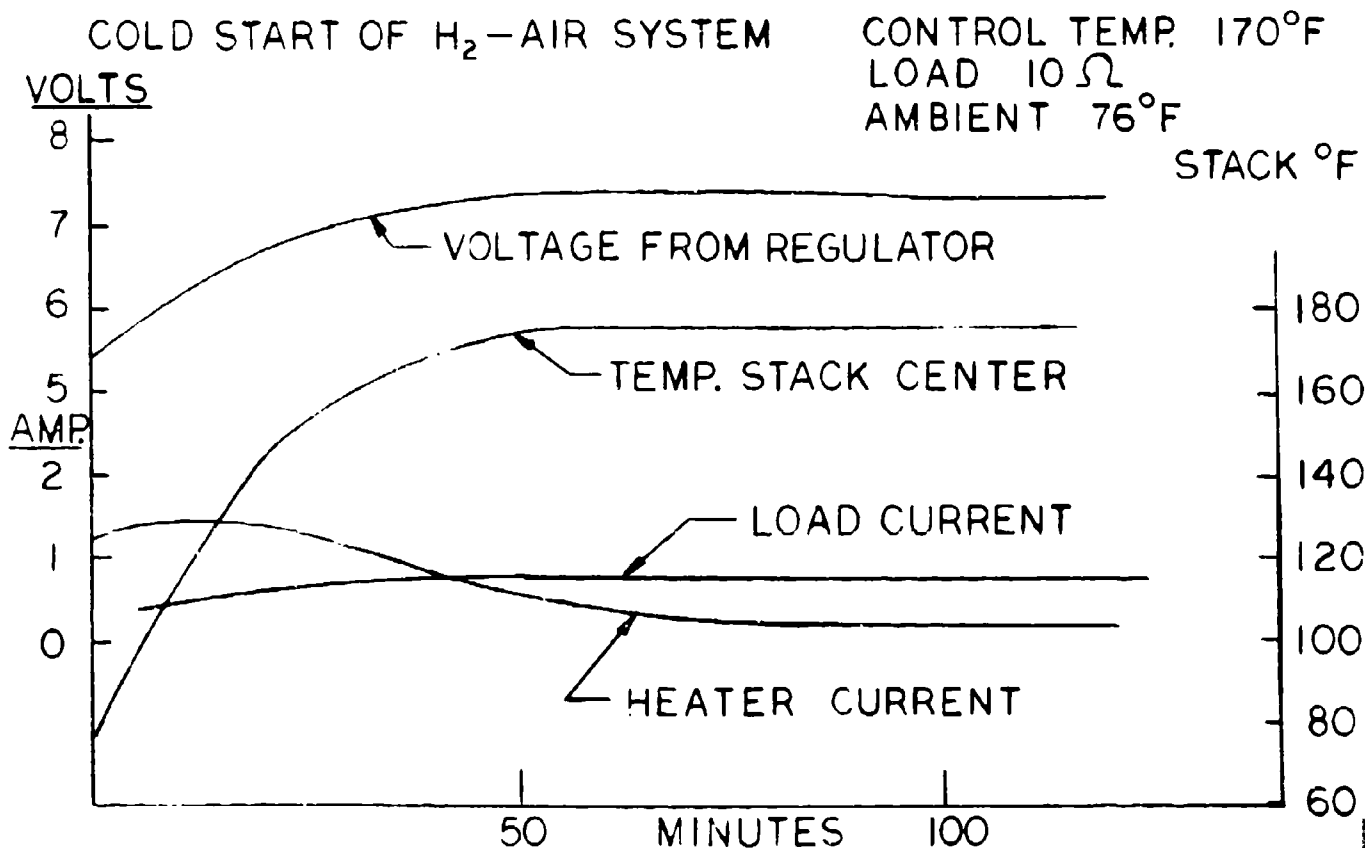   AMBIENT 76°F
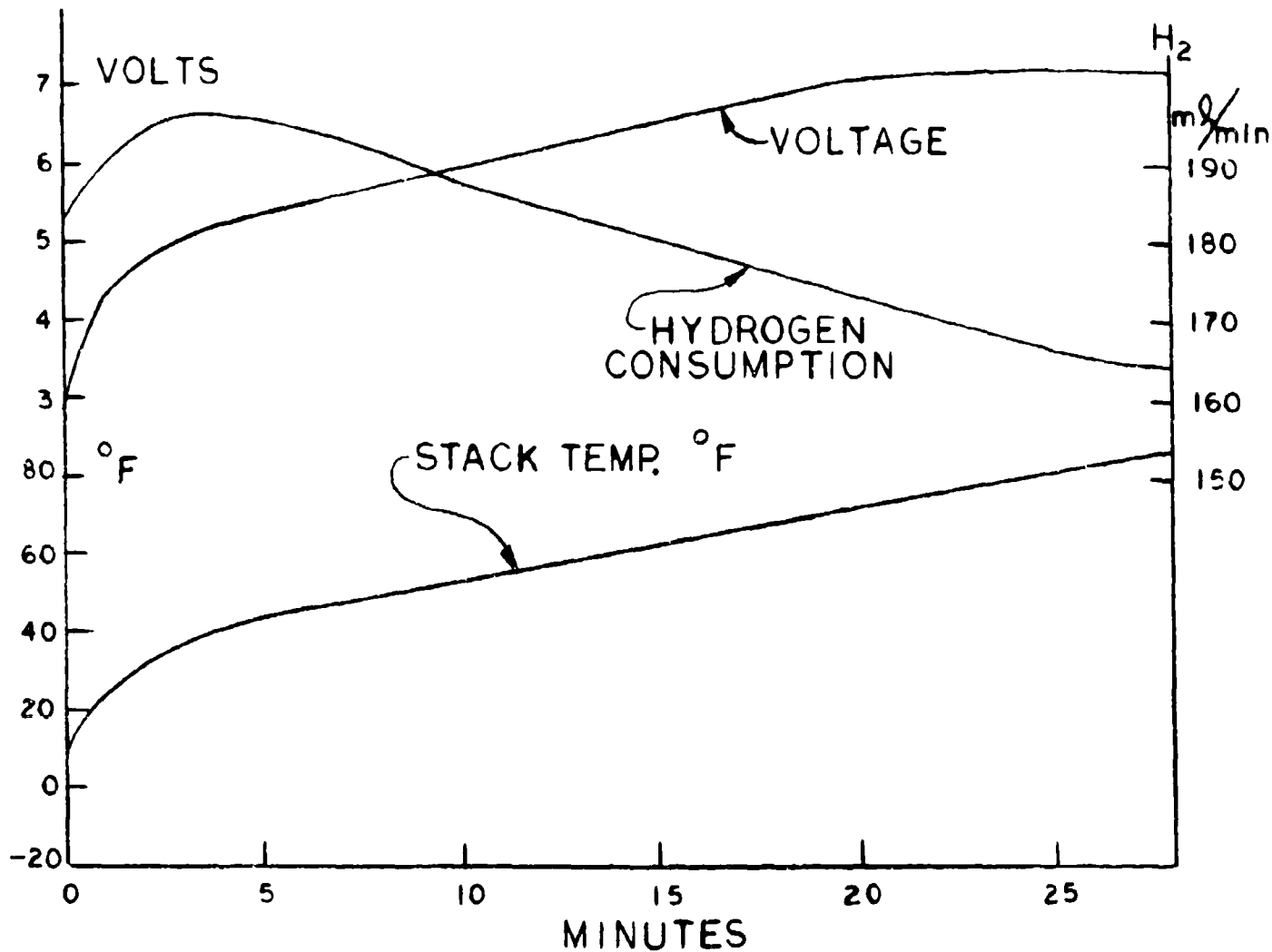
FIG. A-6

6.2.2 EFFECT OF AMBIENT TEMPERATURE

The effect of temperature on performance was studied in the range of 9 to 132°F.

Evaluation data are summarized in Table A-4. Hydrogen consumption and stack temperature were determined for various load conditions.

The tests involved equilibration of the system at the stated ambient temperature followed by a 24 hour evaluation.

Unless otherwise noted, data given in Table A-4 refer to the performance at the end of the 24 hour period.

6.2.3 VOLTAGE RESPONSE

The voltage recovery or decay in a hydrogen-air cell upon load change is mostly instantaneous. Delays can occur because of delays in reactant supply or thermal effects.

Voltage response data were determined for the 5-watt hydrogen-air cell for some extreme operating conditions.

Test information is tabulated in Table A-5. Close voltage regulation is obtained upon load change except when the change is from zero load to full load at low temperature. This is attributed to a temperature gradient which develops in the stack at low temperature.

At zero load comparatively more heat is supplied by endplate heater leaving the stack center cooler. The delay in voltage recovery comes about by the need for heating this portion of the stack.

6.2.4 ENDURANCE TESTING

Life testing was performed on individual stacks as well as fully integrated systems. Tests indicated excellent stability of the cells themself with degradation or failure related to reactant distribution and water balance problems or hydrogen leakage. Performance data for the finalized system as presently developed appear in Table A-7.

TABLE A-5   EFFECT OF AMBIENT TEMPERATURE ON CELL PERFORMANCE

Load	°F Ambient	Volts*	Watts Net	°F Stack Center	H$_2$ Consumption ml/min
0	125-32	7.6	0	137	27
10	127-32	7.6	5.8	173	60
20	132	7.6	2.9	158	117
0	10-14	7.6	0	109	110
10	10-17	7.2	5.2	115	145
20	9-14	7.4	2.7	110	120
10	76	7.5			
20	76	7.5			
0	76	7.6	0	163	100

*After voltage regulation

TABLE A-6   VOLTAGE VARIATION UPON LOAD CHANGE*

*Voltage regulation set to 7.6 volts **5% of
steady state voltage.

Load	°F	Volts Before Load Change	Volts Immediately After Load/chg.	Steady State Volts After/chg.	Recovery Time**
0 to 10	132	7.6	7.4	7.6	0
10 to 0	128	7.6	8.2	7.6	20 sec.
0 to 10	10	7.4	6.8	7.4	16 min.
10 to 0	12	7.4	7.6	7.6	0

TABLE A-7

LIFE TEST WITH 5-WATT HYDROGEN-AIR SYSTEM UNDER OVERLOAD CONDITIONS

Average Load   :   11.3 watts
Hydrogen Pressure: Atmosphoric
Hydrogen Purge   :   2 ml/min.
Air Flow   :   4 1/min.
Control Temperature: 150°F,   Ambient Temperature 73-80°F

Hours	Stack Voltage	Load Current	°F Stack Center
0	6.97	1.66	153
144	6.89	1.66	152
312	6.89	1.66	153
504	6.79	1.66	152
672	6.70	1.60	152
744	6.73	1.60	152
816	6.83	1.63	151
1032	6.78	1.65	152

Hydrogen Pressure 0.3 psig,
Control Temperature 145°F, Ambient: 70-80°F

0	6.96	1.62	140
24	6.98	1.62	142
48	6.98	1.62	143
120	6.86	1.62	138
216	6.89	1.62	140
312	6.84	1.58	145
748	6.65	1.58	145

FIGURE 4

Arrhenius Plot of Deposition Rate of Ta, ▣ , TaC_x, ▲, (gas flow cm^3/min for Ta, 25 HCl, 100 H_2, 200 He, and for TaC_x, 40 HCl, 260 CH_4).
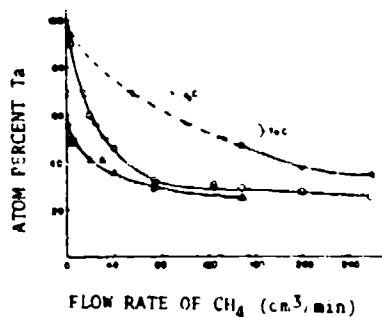

Figure 4 plot: COATING THICKNESS (mils) vs 1000/T°K, COATING RATE (mils/min)

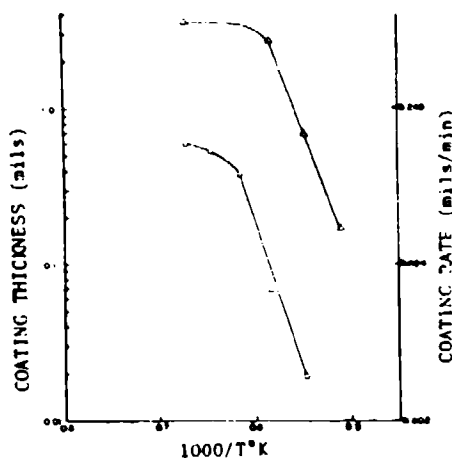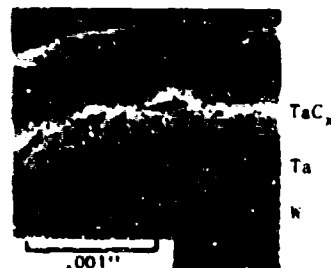FLOW RATE OF CH_4 (cm^3/min) — ATOM PERCENT Ta

FIGURE 5

Effect of Variation of CH_4 in Gas Mixture on the Amount of Ta in TaC_x. (Gas flow cm^3/min, ☉ 40 HCl, 1100°C; ▣ 40 HCl, 950°C. ▲ 20 Cl_2, 1100°C).

FIGURE 6

Deposition Rate of TaC_x for Different CH_4 Concentrations. (Gas flow cm^3/min, ☉ 40 HCl chlorinator, 1100°C. ▣ 40 HCl chlorinator, 950°C, ▲ 20 Cl_2 chlorinator, 1100°C).

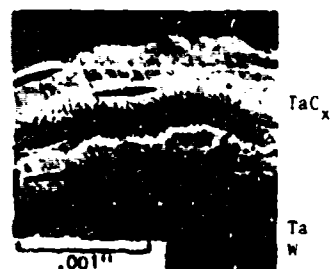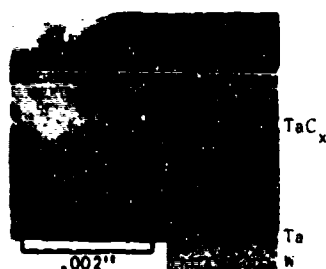Figure 6 plot: COATING THICKNESS (mils) vs FLOW RATE OF CH_4 (cm^3/min), COATING RATE (mils/min)
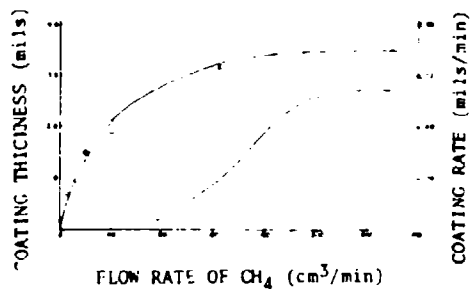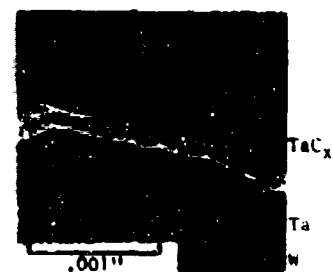
7a: Gas Composition (cm³/min). 5 CH₄, 40 HCl, 255 He. Deposition Rate 0.12 mils/min.

7b: Gas Composition (cm³/min). 20 CH₄, 40 HCl, 240 He. Deposition Rate 0.336 mils/min.

7c: Gas Composition (cm³/min). 30 CH₄, 40 HCl, 230 He. Deposition Rate 0.432 mils/min.

7d: Gas Composition (cm³/min). 200 CH₄, 40 HCl, 60 He. Deposition Rate 0.828 mils/min.

Figure 7. Sectional Views of the TaC_x Coatings Deposited at 1100°C, Using Various Concentrations of CH_4 in the Gas Mixture.